

Activation of carbon suboxide (C₃O₂) by U(III) to form a cyclobutane-1,3-dione Ring.

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Activation of Carbon Suboxide (C_3O_2) by U(III) to form a Cyclobutane-1,3-dione Ring.

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The activation of C_3O_2 by the U(III) complex $[U(\eta^5-Cp')_3]$ ($Cp' = C_5H_4SiMe_3$) is described. The reaction results in the reductive coupling of three C_3O_2 units to form a tetranuclear complex with a central cyclobutane-1,3-dione ring, with concomitant loss of CO. Careful control of reaction conditions has allowed the trapping of an intermediate, dimeric bridging ketene complex, which undergoes insertion of C_3O_2 to form the final product.

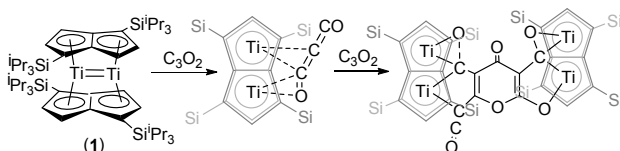
The resurgence of non-aqueous uranium chemistry has led to a wide range of novel reactivity towards many important small molecules.¹ Pertinent examples, encompassing both high and low valent uranium centres, include the reductive homologation of CO,² the reductive coupling of CO_2 ,³ SO_2 ,^{3b} and NO/CO mixtures,⁴ conversion of CO to the isocyanate anion,⁵ the transformation of CO/ H_2 to the methoxide anion,⁶ N_2 activation⁷ and more recently the electrocatalytic splitting of H_2O ⁸ as well as the reduction of N_2 to NH_3 .⁹ However, the interaction of carbon suboxide (C_3O_2) with uranium complexes is as yet unexplored. C_3O_2 is the first in the series of odd carbon chain suboxides that are synthetically available.¹⁰ Its physical and spectroscopic properties have been extensively studied both theoretically^{10c,11} and experimentally.¹² Although its reactivity with many organic substrates is well established,^{12e,13} its coordination chemistry¹⁴ and subsequent metal mediated activation¹⁵ are relatively limited, although the latter have recently been examined *in silico*.^{11a,16} Based on the lack of examples regarding the reactivity of C_3O_2 with uranium

by our recent success in isolating the first structurally authenticated complex of C_3O_2 *en route* to its trimerisation mediated by the syn-bimetallic complex (1) (Scheme 1),¹⁷ we decided to undertake such a study.

Exposure of olive-green brown toluene solutions of mixed sandwich complexes of the general molecular formula $[U(\eta^8-C_8H_6-\{1,4-(SiR_3)_2\})(\eta^5-Cp^{Me4R'})](THF)_x]$ ($R = Me$, $R' = Me$ or iPr , $x = 1$; $R = iPr$, $R' = Me$, $x = 0$ respectively) to C_3O_2 (a very detailed synthesis of C_3O_2 can be found in ref. 17) at $-78^\circ C$ in a 1:1 stoichiometry, resulted in intense brown-red solutions. However, despite our best efforts, work-up under a range of different conditions afforded only intractable solids, that were completely insoluble in common organic solvents. We suspected that the $[COT^{1,4-(SiR_3)_2}]^{2-}$ ($COT = C_8H_6$) ligand might not be inert to attack by C_3O_2 , in contrast to the Pn^+ supporting ligand ($Pn^+ = C_8H_4-\{1,4-(Si^iPr_3)_2\}$) (Scheme 1).¹⁷ Therefore, we decided to turn our attention to another class of U(III) compounds, namely the tris-cyclopentadienyl complexes.

The U(III) complex $[U(\eta^5-Cp')_3]$ (2) ($Cp' = C_5H_4SiMe_3$), first synthesised by Andersen *et al.*,¹⁸ was envisaged as a viable candidate,¹⁹ especially in light of the ability of the Cp' ligand to stabilise low valent U(II)²⁰ and Ln(II)²¹ ($Ln =$ lanthanide) complexes. When a green toluene solution of (2) is exposed to C_3O_2 at $-78^\circ C$ in a 1:1 ratio an instantaneous color change to deep-red wine occurs. Work-up under optimised conditions (see ESI), followed by analysis by 1H -NMR spectroscopy of the crude reaction mixture, showed the existence of a new major species (3) (*ca.* $\geq 70\%$) that displayed two signals in a 1:1 ratio corresponding to two $SiMe_3$ resonances. The $^{29}Si\{^1H\}$ -NMR spectrum also showed only two signals located at -65.60 and -69.57 ppm (δ C_6D_6) shifted downfield from -165 ppm for (2), further signifying a change in the oxidation state of the metal centre.²²

Mass spectrometry was uninformative as only fragments



Scheme 1: Trimerisation of C_3O_2 mediated by (1)

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complexes (or indeed any other f-elements) and encouraged

related to (2) were identifiable. However, crystals suitable for

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an XRD study were eventually obtained from n-heptane (Figure 1), albeit in low yield. Nevertheless, this crystalline material indeed corresponds to the major component of the reaction mixture, as confirmed by its ^1H and $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectra, while its overall symmetry (C_i) is retained in solution and accounts for the observed spectra. **(3)** displays a tetranuclear structure in which four $[\text{U}(\eta^5\text{-Cp}')_3]$ centres are linked by a complex organic structure containing a central

bis($\text{R}_1\text{R}_2\text{ylene}$)cyclobutane-1,3-diones.²⁶ Finally, the C4-C5 bond length of 1.491(5) Å is in excellent agreement with the corresponding C-C bonds found in dispiro[2.1.2.1]octan-4,8-dione,²⁷ dispiro[4.14.1]dodeca-2,9-diene-6,12-dione²⁸ and 1,6-diphenyldispiro[2.1.2.1]octane-4,8-dione²⁹ and the same applies for the C5-O3 bond distance (1.217(5) Å). Based on these metrics, a simplified depiction of the bonding in **(3)** is shown in Figure 2.

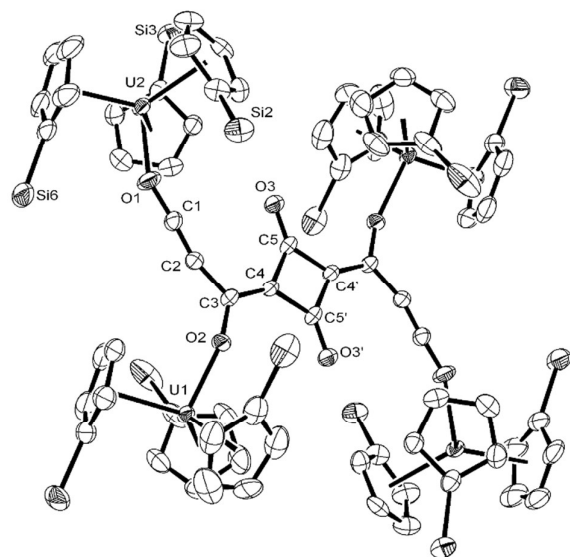


Figure 1: ORTEP diagram of the molecular structure of **(3)**, showing 50% probability ellipsoids. H atoms and methyl groups of the SiMe_3 substituents have been omitted for clarity. The molecule in the unit cell is generated by symmetry (inversion centre) and therefore only bond lengths and angles relating to the labelled atoms are discussed.

cyclobutane-1,3-dione ring; indeed the IR spectrum (thin film) of **(3)** exhibits bands at 1832 and 1733 cm^{-1} characteristic of carbonyl stretches.²³ Inspection of the metric parameters in **(3)** reveals the following salient features. Firstly, the U1-O2 bond is shorter (2.144(3) Å) than the U2-O1 bond (2.264(3) Å); the former is reminiscent of the U-O bonds found in the series of ynediolate complexes of the type $[\text{U}]\text{-O-C}\equiv\text{C-O}[\text{U}]$ (2.101–2.159 Å)^{2c,d,e,g} while the latter is more akin to the average U-O bond distance observed for the complexes in the series $[(\text{U}(\eta^8\text{-C}_8\text{H}_6\{1,4\text{-(SiMe}_3)_2\})(\eta^5\text{-Cp}^{\text{Me4R}''}))_2(\mu\text{-}\eta^1, \eta^2\text{-CO}_3)]$ ($\text{R}'' = \text{Et}, ^i\text{Pr}, ^t\text{Bu}$) (ca. 2.334 Å).³ Similarly the C1-O1 (1.260(5) Å) is reminiscent of the O-C bond length found in the aforementioned ynediolate complexes, while the C3-O2 bond is elongated in comparison (1.321(5) Å), but still at the longer end of the range of C-O bond distances found in ynediolate complexes.^{2c,d,e,g} The C1-C2 bond length of 1.203(6) Å is typical of a triple bond and is in fair agreement with the $\text{C}\equiv\text{C}$ bond observed in ynediolate complexes as well as mono and bis alkynyl complexes of U²⁴, but shorter than the one found in free C_3O_2 in the solid state (1.2564 Å).^{12d} In contrast the C2-C3 bond distance of 1.419(5) Å is typical of a sp-sp^2 σ -bond.²⁵ This is further confirmed by the O2-C3-C2 angle of 118.3(4)°, as well as the C3-C4 bond distance of 1.365(6) Å that is typical of a double bond such as those found in structurally characterised 2,4-

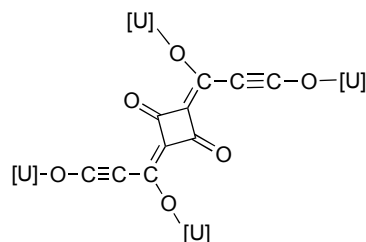
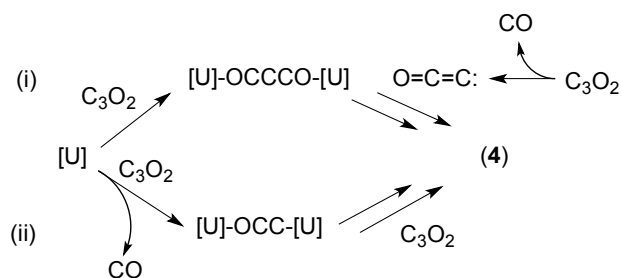


Figure 2. Bonding in **(3)** ($[\text{U}] = \text{UCp}'_3$)

As can be seen from Figure 2, the formation of **(3)** can be rationalised by considering two possible pathways shown in Scheme 2.



Scheme 2. Pathways for the formation of **(3)** ($[\text{U}] = \text{UCp}'_3$)

(i) coordination of a C_3O_2 molecule *via* its O atoms followed by nucleophilic attack at one of its terminal carbons by a ketene fragment generated from the breakdown of C_3O_2 in the presence of a reducing U(III) centre, with concomitant release of CO, or alternatively *via* (ii) insertion of a C_3O_2 molecule in the U-C bond of a $\{[\text{U}]\text{-CCO}[\text{U}]\}$ species ($[\text{U}] = \text{U}(\eta^5\text{-Cp}')_3$). The latter can be seen as a doubly reduced form of ketene and as in the case of pathway (i) means that CO should be produced during the course of the reaction between **(2)** and C_3O_2 . Indeed, the formation of CO was confirmed by GC-MS analysis of the headspace above the reaction mixture. The propensity of C_3O_2 to act as a source of CCO, especially in the presence of phosphine ligands, was observed by Hillhouse *et al.*^{15e} and is probably one of the main reasons which hindered many of the early investigations into its coordination chemistry. In order to investigate the formation of **(3)** more closely, we decided to repeat the reaction between **(2)** and C_3O_2 but this time to remove the volatiles at low temperature (we had previously employed this approach to isolate the first structurally authenticated complex of C_3O_2 supported by **(1)**, Scheme 1).¹⁷ Indeed, removal of volatiles at -60°C followed by ^1H and

$^{29}\text{Si}\{^1\text{H}\}$ -NMR analysis of the resulting deep red wine residue, showed the existence of a new, previously unobserved, major species (**4**) (*ca.* $\geq 70\%$) which featured the same general spectroscopic characteristics as (**3**) (*i.e.* two signals in a 1:1 ratio for the SiMe_3 resonances in the ^1H -NMR spectrum and two resonances at its $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectrum centered at -70.70 and -76.03 δ ppm). Recrystallisation of (**4**) from SiMe_4 , afforded crystals suitable for an XRD study (Figure 3) in moderate yield.³⁰ Compound (**4**) contains a ketene (CCO) ligand bridging two $[\text{U}(\eta^5\text{-Cp}')_3]$ centres and is C_3 symmetric, thus accounting for the observed ^1H -NMR and $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectra. The formulation of (**4**) was confirmed by mass spectrometry (EI) which shows the molecular ion (1340 Da) with the expected isotopic envelope. The formation of (**4**) at low temperatures would suggest that the formation (**3**) proceeds via pathway (ii) (Scheme 2), in which C_3O_2 inserts into the U-C bond in (**4**). Indeed, NMR studies showed that treatment of isolated (**4**) in C_7D_8 with C_3O_2 resulted in quantitative formation of (**3**).

Unfortunately, due to the crystallographic restraints used to refine the model of (**4**) (the molecule is generated by a centre of inversion at C1 leading to mixed occupancy of the O1 and terminal carbon C2 positions), we cannot discuss the bond lengths with the expected level of confidence. Nevertheless, the U2-O1 (and symmetrically related U1-C2) bond distance of

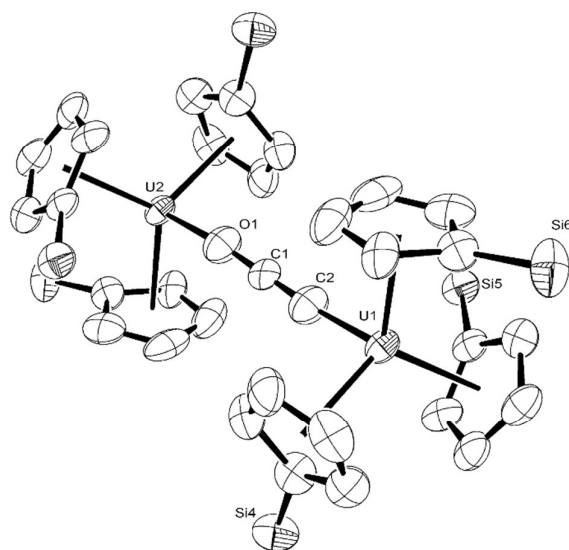


Figure 3: ORTEP diagram of the molecular structure of (**4**), showing 50% probability ellipsoids. H atoms, a molecule of crystallisation solvent (SiMe_4) and methyl groups of the SiMe_3 substituents have been omitted for clarity.

ca. 2.237 Å and C1-C2 distance of *ca.* 1.27 Å are in good agreement with the ones found in reported ynediolate and alkynyl complexes of uranium.^{2c,d,e,g,24} The CCO angle is essentially linear, while the U-O-C (and therefore its symmetry related U-C-C) angle of 165.5° is in the same range as the ones found in sterically encumbered ynediolate and alkynyl complexes of uranium. Despite this disorder we are confident as to the nature of the CCO linker based on the spectroscopic evidence discussed above, and that (**4**) contains a two U(IV) centres bridged by a doubly reduced ketene unit (*i.e.* $[\text{U}]\text{-O-}$

$\text{C}\equiv\text{C-}[\text{U}]$). The IR spectrum (thin film) of (**4**) displays a strong band at 2010 cm^{-1} which we assign to the $\text{C}\equiv\text{C}$ stretch in the latter.³¹

In conclusion, we report the first example of the activation of C_3O_2 by a U(III) complex, which affords a cyclobutane-1,3-dione derivative (**3**). In the presence of the reducing U(III) centre, C_3O_2 decomposes to CO and ketene, and under carefully controlled conditions, the ketene can be trapped to afford the di-uranium bridging ketene complex (**4**). The latter then undergoes insertion of further C_3O_2 into its U-C bond to ultimately yield (**3**).

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Conflicts of interest

There are no conflicts to declare.

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$[\text{U}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_3]$ reductively couples three C_3O_2 molecules to form a tetranuclear complex with a central cyclobutane-1,3-dione ring, via an intermediate bridging ketene complex.

